



One-step synthesis of pH-sensitive poly(Acrylamide-co-Sodium Acrylate) beads with core-shell structure

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ARTICLE INFO

Article history:

Received 23 May 2012

Received in revised form 13 August 2012

Accepted 16 August 2012

Available online 24 August 2012

Keywords:

Hydrogel beads

Core-shell structure

Phase separation

pH sensitive

ABSTRACT

This work describes a novel one-step method to prepare poly(AMm-co-AAcNa) pH-sensitive hydrogel beads with core-shell structure induced by a spontaneous phase separation process during polymerization. In virtue of the phase separation process, polymers with high molecular weight separate to the core phase whereas monomers are left in the shell. This redistribution inside the droplets enables the polymerization environment change sharply to endow the beads with different network structure in core and shell. FTIR spectrum and EDS show that core and shell share identical composition; yet GPC exhibits a bimodal molecular weight distribution which lead to a conventional network in core but a rich-in-branch network in shell. This difference in structure results in mainly three discrepancies in performance. The level of volume change that the beads exhibit at about pH = 4 is much more intense for shell than for core; the swelling/shrinking kinetics of the core and shell indicates that shell responses about 30 times faster than core does; fitting of the absorbency capacity exhibited that the ones of the core and shell are about 67 g/g and 2126 g/g, respectively. A microfluidic device with co-axial channel structure is introduced in this fabrication. The hydrogel beads exhibited narrow size distribution and the diameter of core and shell could be freely controlled by the high controllability of microfluidic technology and by manipulating the phase separation process. In sum, this method impart us an easy and fast-running way to obtain hydrogel beads with core-shell structure, which has potential in various applications like optical material, lenses and sensors.

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1. Introduction

Hydrogels are three-dimensional hydrophilic polymer networks that can absorb a large amount of water in their swollen state due to the moderately cross-linked structure. Since the specific chemical functional groups or adjustable crosslink, the swollen state of hydrogels can significantly change by absorbing or expelling water in response to external environmental changes, including ionic strength or pH [1,2], temperature [3,4], substrate concentration [5–7], electric signal, light, etc. These materials were also called smart hydrogel, intelligent hydrogel, or stimuli-responsive hydrogel. In last decades, great attentions have been focused on stimuli-responsive hydrogel materials since their preponderant properties in medical fields [8–10], sensors [11,12], chemical separation [13,14], etc.

Hydrogel beads or spheres have been recognized as one of the most potential form amid hydrogel materials because of their regular shape [15–17]. In particular, hydrogel beads with core-shell structure show a promising future in increasingly complicated applications such as drug delivery nowadays, since researchers can assign diverse properties to core and shell to achieve flexible

functionalization. Conventional methods of fabrication of hydrogel beads with core-shell structure are usually composed of two steps or more [18–20], that is selection of substances with functional groups, preparation of the core beads, and coating of the core to form a shell. Although beads or spheres with elaborate core-shell structure, even multiple core-shell structure, might be obtained by manipulating this method, it still seems intricate and time-consuming. Moreover, the adaptable cores are usually lack of stimuli responses for a fine coating. There might be some distinctive ideology to fabricate hydrogel beads with core-shell structure.

Liquid-liquid phase separation (LLPS) system has presented large numbers of opportunities to handle polymerization process to achieve diverse configurations of polymers [21], such as microgel and scaffolds with porous structure. Three prevalent methods were widely reported: precipitation polymerization [21], dispersion polymerization [22,23], and a recent developed aqueous-two-phase system (ATPS) polymerization [24]. The mechanism of all these methods may be attributed to the selection of the medium as a good solvent of monomers but non-solvent for polymers [25,26]. Therefore, phase separation will happen with the proceeding of polymerization. Manipulation of the thermodynamics and kinetics of phase separations leads to a wide variety of morphologies of the structures.

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Dalton [27] fabricated a macroporous poly-Hydroxyethyl methacrylate (PHEMA) hydrogel tube with beaded morphology. This structure is formed by coalescence of aggregated microparticles formed under precipitation polymerization conditions. Shan et al. [24] carried out polymerization of acrylamide (AMm) in polyethylene glycol (PEG) + polyacrylamide (PAM) + H₂O system. Once the macroradicals of AMm in the PEG solution attained a critical chain length, they separated from PEG solution and finally aggregated to form PAM beads. Different from the conventional emulsion polymerization for hydrophobic polymer beads preparation, such a process is attributed to APTS polymerization, where PAM beads contain large amount of water as hydrogel material. Based on LLPS mechanism, dextran microspheres were fabricated by Stenekes et al. [28] in aqueous solutions of PEG and methacrylated dextran.

Up to date, most of reported polymerization processes involving LLPS were exploiting only one of the two separated phases as products. For instances, the continuous phase was served as dispersant to obtain microspheres and particles of the dispersed phase, or the dispersed phase was served as templates to achieve bulk materials with porous structure. While in an LLPS polymerization process, water can be redistributed once the phase separation happens, which may enable the polymerization environment change sharply to obtain polymeric material different from the origin. Thus, if we carry out LLPS polymerization process during preparation of hydrogel materials and retain both phases after separation, we might obtain heterogeneous hydrogel materials.

Evidently, the droplet size distribution is critical for controlling the size, morphology and performance of polymer beads when introducing a polymerization process within droplets. However, monodispersed droplets are favorable. In recent, microfluidic technique has been highly focused on because of its safety, high efficiency, repeatability, and facile flow controllability in manipulation on multiphase flow [29,30]. Monodispersed droplets in micron scale can be easily prepared by microfluidic technique. In addition, carried by the flowing continuous phase fluid, these droplets can experience a strictly controlled residence time, and exchange heat with the continuous phase fluid promptly [31,32]. Considering these characters, we believe that functional hydrogel preparation process may be finely controlled in droplets generated by microfluidics technologies under a wider range of experimental conditions.

In this work, based on the mechanism of polymerization induced LLPS, we describe a facile process to attempt continuous fabrication of poly-(Sodium Acrylate-co-Acrylamide) (P(AAcNa-co-AMm)) hydrogel beads with core-shell structure by one-step suspension polymerization in water droplets containing AAcNa and AMm, redox initiator pair of ammonium persulfate (APS)-N,N,N',N'-tetramethylethylenediamine (TEMED) and crosslinker N,N'-methylenebisacrylamide (MBA). A co-axial microfluidic device was employed to make this polymerization process under control even if the monomer concentration and ambient temperature were set at relative high levels. The compositions of the core and the shell were comprehensively examined to understand the generation mechanism of the core-shell structure. The water capacity and the pH-sensitivity of core and shell were also tested with respect to the changing of reaction temperature and initial reactants composition for further exploration in applications.

2. Materials and methods

2.1. Materials

Acrylamide (AMm) and N,N'-methylene-bis-acrylamide (MBA) were purchased from Biodee (China). Ammonium persulfate (APS), N,N,N',N'-tetramethylethylenediamine (TEMED), Acrylic acid (AAc), Sodium Hydroxide (NaOH), Hydrochloride (HCl, aqueous solution, 37 wt.%) and sodium chloride (NaCl) were purchased from

Sinopharm (China). All these agents were used as received. AAcNa was obtained by neutralizing AAc with NaOH, and then recrystallized twice from deionized water before used. NaCl aqueous solution of 0.1 mol/L was made up with deionized water for adjusting the ionic strength in experiments. Buffer solutions with pH values of 2.1 and 7.2 were prepared by blending NaH₂PO₄, Na₂HPO₄, and H₃PO₄ quantitatively and the ionic strengths of each buffer was adjusted to 0.01 mol/L.

2.2. Microfluidic device and fabrication method

The schematic diagram of the experimental device is shown in Fig. 1. A co-axial microdevice was used to control the liquid-liquid dripping flow, which was fabricated on two polymethyl methacrylate (PMMA) plates with an end mill and sealed by high pressure thermal sealing techniques. The main channel embedded in the PMMA scaffold was a PTFE tube 5 m in length with outer and inner diameters of approximately 600 μm and 1.0 mm, respectively. A quartz capillary tube (ID 200 μm, OD 320 μm) for injecting the dispersed phase was inserted into the PTFE tube to form a co-axial geometry. Two needles with outer diameter of 0.8 mm were fixed vertically to the main channel for introducing the continuous phase.

The dispersed phase was an aqueous solution containing monomer (AMm and AAcNa), crosslinker (MBA), initiator (APS) and accelerator (TEMED). The total concentration of monomer was fixed at 4.2 mol/L, while the mole ratio of AAcNa to AMm was adjusted from 10:0 to 0:10. The dispersed phase solution without TEMED was purged with nitrogen gas for 20 min as prepared and kept at 4 °C, while TEMED was added to form a redox initiator pair just before polymerization. The standard recipe of ingredients is shown in Table 1, in which the amount of crosslinker and initiator were calculated with respect to monomers. The continuous oil phase was mixture of *n*-octane and paraffine with the mass ratio of 4:6.

Two microsyringe pumps and three microsyringes were used to pump the two phases into the microfluidic device. The flow rates of the dispersed and continuous phase were 30 and 600 μL/min, respectively. The dispersed phase droplets were generated from the sheath shear flow in the co-axial geometry at room temperature and flowed forward along the microchannel together with the continuous phase. A thermostat with an accuracy of 0.1 K was used to heat fluids flowing from 80 to 95 °C through the PTFE tube to realize in situ radical polymerization within the droplets. The length of the PTFE tubing immersed in the heat bath was adjusted to provide a 2 min residence time at high temperature for each droplet to undergo polymerization.

After polymerization, a vessel containing two separated phases of oil and deionized water was used to collect the products at the outlet of the PTFE tube. Hydrogel microspheres passed through the oil phase and into the water phase by sedimentation. The products were then removed to rinse by deionized water thrice for further characterization.

2.3. Characterization

2.3.1. Observations

A vertical microscope at magnification from 50× to 200× was used to observe the droplets and hydrogel beads. Pictures were caught by a frequency of 200 per second by a CCD connected to the microscope. The diameter of droplets and hydrogel beads were measured with the aid of image analysis software. Each point we sketched in figures below was determined by measurement of more than 20 droplets or beads randomly.

Scanning electron microscope (SEM) JEOL 7401F JEOL, Japan) was used to characterize the microscopic structure of the hydrogel beads. The specimens were prepared for SEM by freeze-drying and applied a gold coating of about 150 Å.

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